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Adsorption of Thiol-Containing Copolymers onto Gold

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ABSTRACT: Polystyrene and poly(styrenesulfonate) copolymers bearing (mercaptomethyl)styrene units have been synthesized *via* an amidinothio intermediate which allows for quantitative hydrolysis to the thiol. The kinetics of adsorption of these polymers to gold has been determined *in situ* using the quartz crystal microbalance. The introduction of a few percent of thiol groups causes polystyrene to adsorb to gold from a good solvent (THF). Poly(styrenesulfonate) can also be induced to adsorb at a negatively charged (repulsive) gold/water interface when heavily loaded with (mercaptomethyl)styrene. Copolymers adsorb relatively rapidly, attaining stable surface coverages within 1 h. Steady-state adsorbance for copolymers of wide molecular-weight distribution is taken as indirect evidence for adsorption in the nonequilibrium regime. Electron spectroscopy of adsorbed poly(styrenesulfonate) copolymers suggests that sulfonate groups are expelled from the metal/polymer interface. The kinetics of octadecanethiol chemisorbing to gold was studied to provide a well-characterized, small-molecule comparison.

Introduction

Polymers are known to adsorb in the strong affinity limit, reflected by a sharp increase in surface coverage at low concentrations.[1−4] In addition to polymer adsorption isotherms, there is much interest in the conformation of adsorbed macromolecules, as manifest by the dependence of film thickness or surface coverage on molecular weight, solvent quality, and electrolyte concentration. In the thermodynamic (reversible) limit the conformation of adsorbed polymers tends to be controlled by the strength of segment/surface interactions.[5,6] In the classical loop−train−tail model, strong interaction leads to adsorption in a flat configuration with many trains, whereas weak adsorption affords many loops.[7−9]

The mode of adsorption is also dependent on molecular architecture. Chains may be designed to contain weakly-interacting or noninteracting units copolymerized (random or blocklike) with strongly interacting segments. For example, there has been much recent interest, from practical and theoretical standpoints, on end-attaching polymers.[10−12] Charged and uncharged poly(ethylene oxide)/polystyrene diblock copolymers provide instances where long- and short-range interactions in the physisorbing category are responsible for adsorption and brush formation.[13−17] In these structures, crowding prevents collapse on immersion of the brush in a nonsolvent, or electrolyte (in the case of polyelectrolyte brushes), and layer thickness is proportional to the degree of polymerization.[17−20]

Chemisorption, as exemplified by the sulfur/metal interaction, is a strong, short-range, specific force. There has been intense interest in this type of interaction as a result of the propensity of thiol-containing molecules to form, spontaneously, ordered monolayers (to "self-assemble") at metal surfaces.[21−27] Recently, this type of interaction has been extended to polymers. Polystyrenes with terminal thiol groups were prepared by Stouffer and McCarthy[28] and were shown to adsorb to gold from good solvents. More recently, adsorbed triblock copolymers having thiol segments were shown to induce co-adsorption of charged lipids.[29] Polyacrylate copolymers containing thioethers[30] or disulfides[31] were also found to self-assemble on gold.

Table 1. Polymer Data

polymer[a]	composition	$10^{-3}M_w$	M_w/M_n	T_g, °C
PS	$(C_8H_8)_n$	234	2.6	98
PTMS	$(C_9H_{10}S)_n$			
PS/1% SH	$[(C_8H_8)_{0.992}(C_9H_{10}S)_{0.008}]_n$	127	2.5	93
PS/5% SH	$[(C_8H_8)_{0.946}(C_9H_{10}S)_{0.054}]_n$	304	4.3	103
PSSA	$(C_8H_8SO_3)_n$	70	2.4	
PSSA/65% PTMS	$[(C_8H_8SO_3)_{0.35}(C_9H_{10}S)_{0.65}]_n$	~100		103

[a] PS = polystyrene, PSSA = poly(styrenesulfonate), PTMS = poly((mercaptomethyl)styrene).

In this paper we describe the synthesis of random thiol-containing polystyrenes and their adsorption kinetics to gold. Polymers, both hydrophobic and hydrophilic (polyelectrolytes), were chosen to show how the incorporation of a strongly-chemisorbing group can overcome both the entropy loss of a polymer adsorbing from a good solvent and the electrostatic repulsion of a polyelectrolyte adsorbing at a like-charged surface. The surface coverage was determined *in situ* using the quartz crystal microbalance, which we recently applied to studies of polystyrene adsorption from a Θ solvent.[32]

Results and Discussion

Polymer Synthesis. The composition of homo- and copolymers is given in Table 1. Radical homopolymerization of 4-[(amidinothio)methyl]styrene salt in ethanol proceeded smoothly to yield a water-soluble, hygroscopic polyelectrolyte (Scheme 1). Hydrolysis of the polyelectrolyte afforded partially cross-linked poly((mercaptomethyl)styrene). It is well-known that thiols form disulfides under basic conditions in the presence of oxygen and, although efforts were made to rigorously exclude oxygen during hydrolysis, the resulting polymer apparently contained a small number of disulfide crosslinks. Thus, the material was observed to dissolve only in hot DMF (hydrolysis of polyelectrolyte without exclusion of oxygen afforded insoluble product). The problem of cross-linking is, no doubt, exacerbated by the proximity of thiol groups on the polymer backbone. Styrene copolymers having dilute thiol pendant groups (1%, 5%) were soluble and stable for weeks, after which time slow

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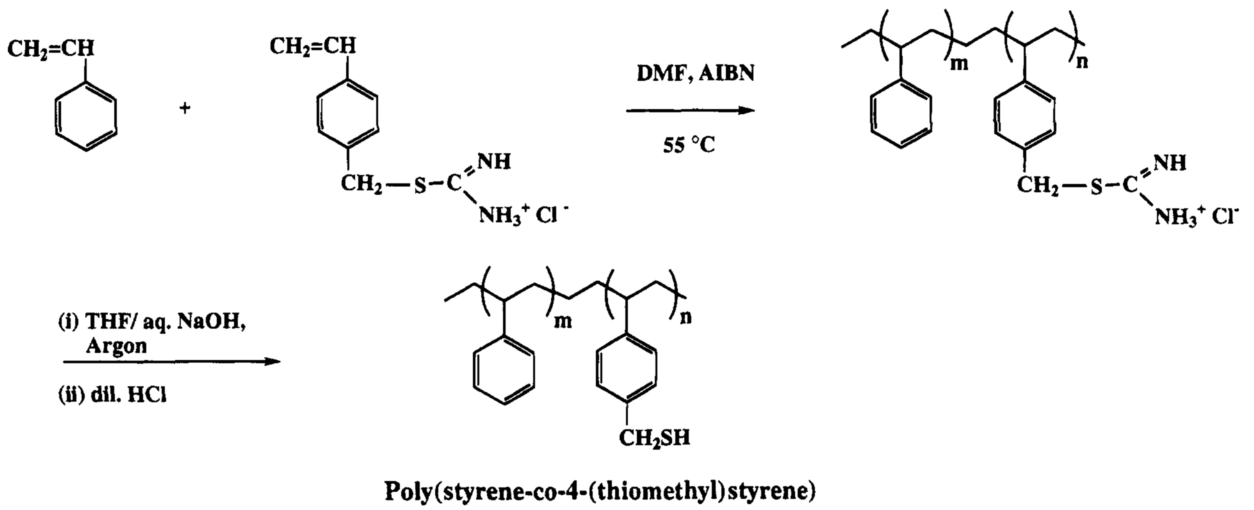
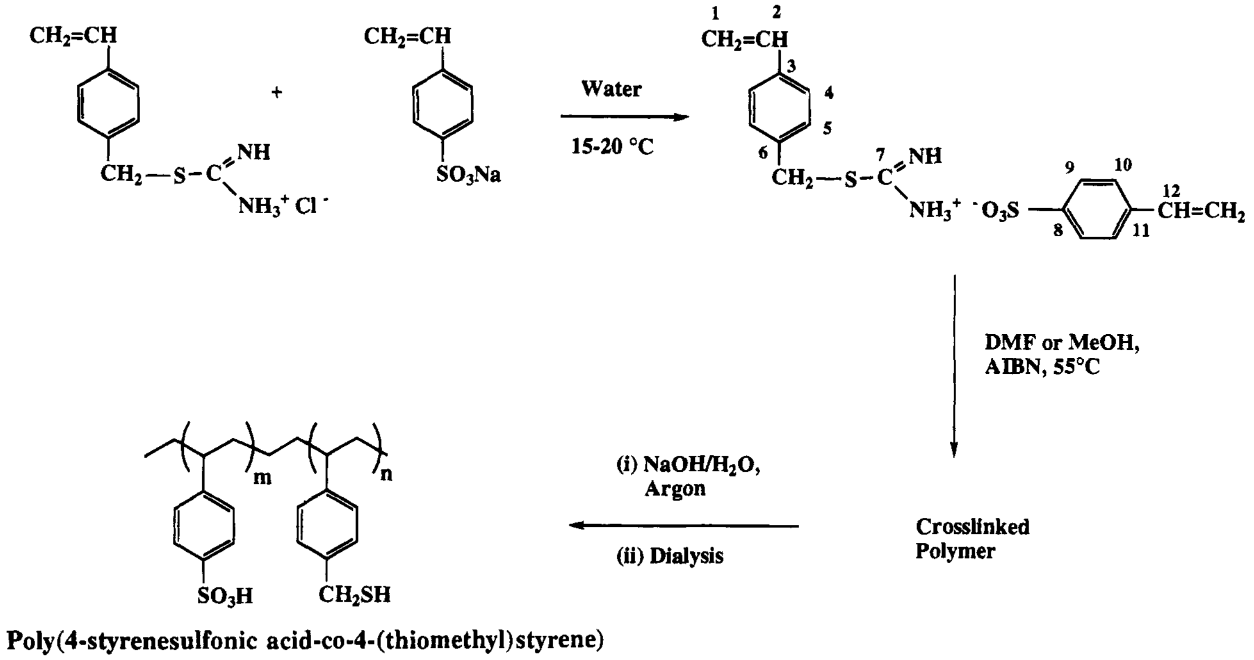
Scheme 1



Scheme 2



cross-linking and precipitation were observed. Since the unhydrolyzed amidinothio copolymer is stable, it is recommended that it be hydrolyzed just before use.

Although the problem of cross-linking can be circumvented with the use of disulfide[31] or thioether-containing[30] pendant groups, there are drawbacks to this strategy. Thiols are known to adsorb rapidly, whereas less is known about the propensity for thioethers to adsorb. In addition, thioether and disulfide polymers contain a short alkyl moiety which must be accounted for after the adsorption process.

An alternative route to poly((mercaptomethyl)styrene) would be to derivatize the corresponding poly(4-(chloromethyl)styrene), as done for the modification of cross-linked resin beads.[33] In our hands this approach yielded approximately 90% conversion of 50 000 molecular-weight poly(4-(chloromethyl)styrene). Reactions on polymers typically have lower yields than the same reaction on small molecules. In comparison, hydrolysis of radiolabeled polyelectrolyte made from 4-[([^{14}C]amidinothio)methyl]styrene hydrochloride showed 99% efficiency (99% decrease in the specific activity of the [^{14}C]amidinothio polymer). As studies on end-attached polymers show,[28] it is critical to have complete derivatization, since the presence of even one strongly-interacting group is sufficient to induce adsorption of a polymer from a good solvent.

The intermediate polymer made from 4-[(amidinothio)methyl]styrene/4-styrenesulfonate (an amphiphile salt) was necessarily physically cross-linked due to electrostatic interaction between positive and negative groups (Scheme 2).

Although the feed ratio of positive and negative monomer is ensured to be 1:1 through the use of this salt, the composition of the hydrolyzed polymer was determined to be *ca.* 35% sulfonate and 65% thiol. Elemental analysis of hydrolyzed polymer indicated partial retention of NaCl following dialysis, as well as some water. The polymer was water soluble and more stable in solution than the uncharged copolymers described above. GPC of the sulfonate/thiol copolymer proved problematic, as is often the case with polyelectrolytes. Partial success in the use of a styrene/divinylbenzene GPC column with DMF as eluent was attained by precipitating the polyelectrolyte from water with 1-(amidinothio)octane hydrobromide salt, which rendered the polymer organic soluble. This counterion-exchange approach to GPC has been taken previously.[34]

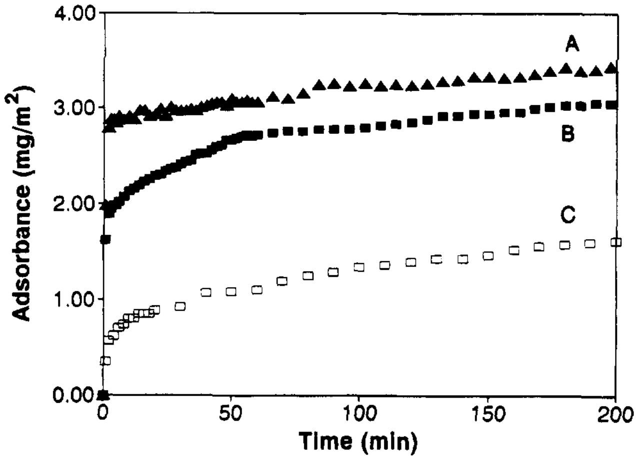


Figure 1. Adsorption of octadecanethiol onto gold at 30 °C. Adsorbance values have not been corrected for a surface roughness factor of *ca.* 1.7: (A) 5 mM octadecanethiol in hexane; (B) 1 mM in hexane; (C) 1 mM in ethanol.

When compared to counterion-exchanged poly(styrenesulfonate) standards the molecular weight was determined to be *ca.* 10^5. The facts that the polymer was retained by 12 000 molecular-weight-cutoff dialysis tubing and that free-standing films could be cast are also indicative of reasonably high molecular weight.

Small-Molecule Adsorption. Initial experiments focused on the adsorption of octadecanethiol to validate the use of the QCM as an experimental tool for our studies and to provide a small-molecule comparison for the adsorption kinetics. Alkanethiols are known to self-assemble rapidly at clean noble metal surfaces. In the case of octadecanethiol ($C_{18}H_{37}SH$) a hexagonal close-packed monolayer is formed on Au[111].[35-37] Although the surface packing and properties of alkanethiol monolayers have been examined in detail, studies of the kinetics of alkanethiol adsorption have been sparse.[22,38,39] Our *in situ* results (Figure 1) confirm much of what is known about $C_{18}H_{37}SH$ adsorption kinetics: adsorption is initially rapid and is followed by a slow period, perhaps involving "reorganization" to maximize packing density[22] and to allow chains to adopt an extended conformation.[39] Also evident is that a higher concentration of thiol leads to faster adsorption and that adsorption from ethanol is slower than from hexane. The surface coverages for adsorption from hexane also tended to be higher than those from ethanol at long times, possibly due to dissolution of gold from the surface (which would decrease the mass of the oscillator and yield lower apparent adsorbance). Using a surface roughness factor of 1.7, determined with ^{35}S-radiolabeled octadecanethiol,[40] for these as-evaporated gold films, one would expect a theoretical adsorbance of 3.2 mg m^{-2} for close-packed C_{18} alkanethiol, approximately the value observed here.

Polymer Adsorption. When polymer is added to a QCM immersed in solvent, frequency shifts may be caused both by polymer adsorption and by changes in the viscoelastic properties of the contacting solution.[41,42] This viscosity effect was previously considered in detail and shown to be negligible for the concentration and molecular-weight ranges used in this study.[32]

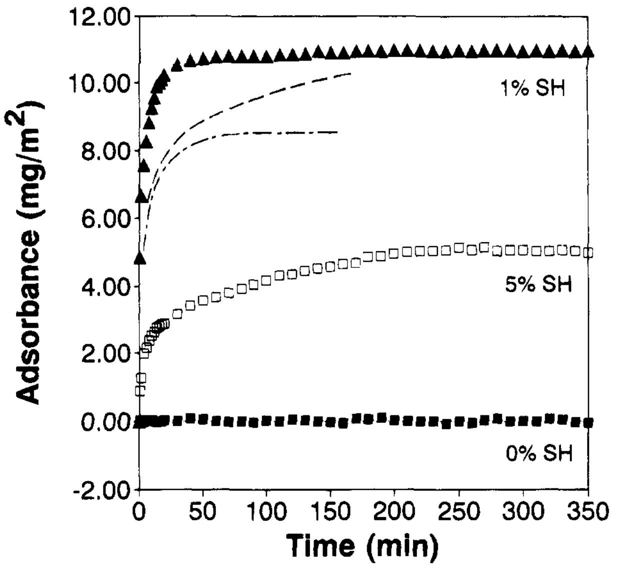


Figure 2. Adsorption of poly(styrene-*co*-(mercaptomethyl)styrene) polymers on gold from THF at 30 °C. Concentration: 0.001 g/100 mL. Nominal compositions are indicated. Also depicted are kinetics for wide-molecular-weight-distribution (M_w = 234 000, M_w/M_n = 2.6) (– – –) and narrow-MWD (M_w = 929 000, M_w/M_n = 1.06) (– • –) polystyrene adsorbing to gold from cyclohexane at 35 °C (Θ solvent). Not corrected for surface roughness.

As shown in Figure 2, polystyrene does not adsorb to gold from THF, a good solvent, as observed previously.[28,43] The introduction of a small percentage of thiol groups causes the polymer to adsorb (Figure 2). It is interesting to note that the coverage for the polymer containing more thiol is **lower**. This is to be expected if thiol groups are surface localized, and the balance of the material is contained in loops dangling off the surface. An expression for the coverage, A (in g cm^{-2}), as a function of surface density of chemisorbed "sticky" feet, σ_s (no. of adsorbed sulfurs cm^{-2}), is easily derived

$$A = \frac{\sigma_s}{fL}\left(M_f + \frac{M_l m}{n}\right) \qquad (1)$$

where M_f and M_l are the molecular weights of a foot and an unbound repeat unit, respectively, n and m are the mole fractions of each, L is Avogadro's number, and f is the fraction of thiols bound to the surface. In the absence of an analytical technique that would yield an estimate for f, only σ_s/f may be determined from the present data. Unless otherwise stated, we will assume f to be 1, supported by theory[44] that predicts the fraction of segments in surface-bound trains to be close to 1 for strong adsorbers. Lenk et al., for self-assembled films of sulfur-derivatized poly(methyl methacrylates) on gold,[30] also found an inverse relationship between film thickness and sulfur density. They ascribed this observation to the relative rates of adsorption *vs* chain spreading on the surface, where more attachment points per molecule preclude displacement by other segments. Their adsorption scheme included a significant fraction of sulfur that was not attached to the surface.

An important question in considering the adsorption characteristics of polymers containing strongly-adsorbing groups is whether the surface coverage is, in fact, under thermodynamic control. For example, extremely long-lived nonequilibrium states of surface composition have been observed experimentally when homopolymer chains adsorb competitively,[45] and for diblock copolymer adsorption "isotherms".[14] The adsorption behavior of the polymers described by Lenk et al.[30] also fall under kinetic control, where subtleties such as solution concentration determine surface coverage. For our styrene/(mercaptomethyl)styrene copolymers, coverage eventually reaches a very stable plateau (Figure 2). The behavior of our copolymers may be contrasted with that for polystyrene adsorption from a Θ solvent.[32] Also indicated in Figure 2 are the QCM adsorption results for narrow- and wide-molecular-weight-distribution (MWD) polystyrene adsorbing onto gold from cyclohexane at 35 °C (Θ solvent). The adsorbance for the wide-MWD polystyrene continually drifts upward, suggesting continual displacement of smaller polymer chains by larger ones,[4] whereas the narrow-MWD polymer reaches a stable limiting value. Since the (wide MWD) thiol copolymer adsorbances rapidly attain stable values, we assume that surface coverage is under *nonequilibrium control*—whatever arrives first at the surface sticks. This type of behavior is to be expected with a macromolecule containing many strongly-chemisorbing segments. An alternative explanation would be that surface coverage of the thiol compolymers has absolutely no dependence on molecular weight, a characteristic we consider to be unlikely.

The configuration of polymers adsorbing irreversibly and reversibly with strong interaction was considered by Konstadinis et al. using dynamic Monte Carlo simulations.[44] They showed that for irreversible surface/segment interactions the adsorbed material exists mostly in trains with no tails. For reversible adsorption of energy $>\sim 2kT$ nonequilibrium effects become significant and adsorbed trains become trapped in nonequilibrium states with the fraction of segments in trains approaching the value for irreversible adsorption (*ca.* 0.9). These findings must be translated to copolymers containing strong adsorbers. For our polymers, since the interaction energy of the sulfur–gold bond[46] is very high on these energy scales (30 kcal mol^{-1} would be *ca.* $50kT$), the adsorption of thiol repeat units may be considered irreversible. Further evidence of irreversible type adsorption comes from studies of redox-tagged alkanethiols[47] and radiolabeled alkanethiols,[40] where exchange experiments have shown desorption to be very slow, with rate constants of the order of 1 day^{-1}. On the time scale of our experiment (Figure 2) a foot would not detach for optimal (re)placement. Slow desorption would contribute to the observed long-time evolution of structure in alkanethiol monolayers.[39] The finding that the 5% copolymer takes longer to reach a limiting coverage (Figure 2) may indicate the existence of some disulfide cross-links, which would take longer to cleave and adsorb to gold. In fact, it may be conducive to denser packing to use a polymer with a few faster-adsorbing thiols mixed in with more slowly-adsorbing disulfides or sulfides.

If we assume that the styrene units all exist in loops, and that most thiols find their way to the surface ($f = 0.9$ from ref 44), and a surface roughness factor of 1.7, the density of sulfur "feet" for the 1% thiol copolymers (using eq 1 and Figure 2) would be *ca.* 3×10^{13} cm^{-2} or about 5% of the density for alkanethiol chains.[36] For the 5% polymer the density would be about 6×10^{13} cm^{-2}. Corresponding areas per foot would be 315 and 170 Å^2, respectively. The average distance between feet would be 18 and 13 Å. The adsorbed layers would thus be quite "porous" to neutral molecules,[30] although the inter-sulfur distance on the surface is much less than the contour length along the backbone from thiol to thiol (220 Å for 1% and 44 Å for 5% copolymer), suggesting reasonably close packing.

The water-soluble polyelectrolyte examined in this work was poly(styrenesulfonate), which did not adsorb to gold (Figure 3). Since the polyelectrolyte is charged, Coulombic interactions between the surface and the polymer must be considered. For example, if the surface were positively charged, the polymer would experience attractive forces. While no attempt was made to control the surface charge of the gold, it was found to adsorb cations in its as-immersed state. We assume that in the KCl electrolyte chloride ions are adsorbed[48] (for an electrochemical study of halide adsorption see: Lingane, J. J. *J. Electroanal. Chem.* **1962**, *4*, 332), which induces coadsorption of cations for charge neutrality. Anion adsorption onto noble metals with concomitant metal ion co-adsorption is well documented.[49-51] The extent of cation adsorption was assayed by adsorbing lead ions from an aqueous solution of lead perchlorate or lead chloride. A frequency change of 6 Hz upon lead adsorption yields a surface coverage of *ca.* 1×10^{14} cations/cm^2. A monolayer of lead ions with effective radius of 4.5 Å would have a density of *ca.* 1.2×10^{14} cm^{-2}, coadsorbed with twice as many chloride ions.

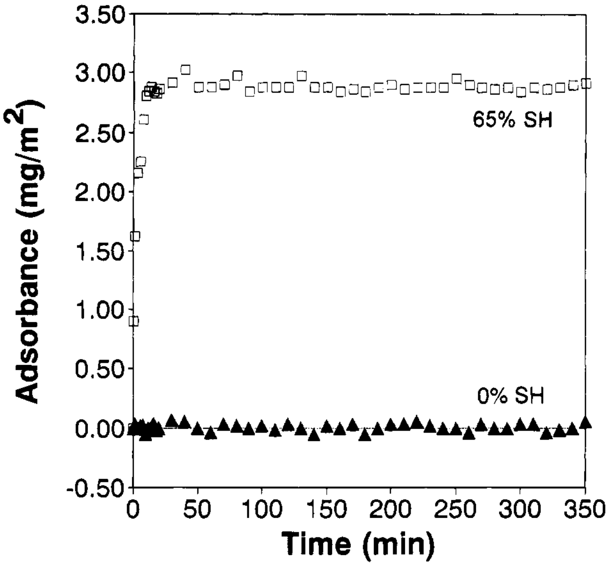


Figure 3. Kinetics of adsorption of poly(styrenesulfonate) and poly(styrenesulfonate-*co*-(mercaptomethyl)styrene) onto gold from aqueous 0.1 M KCl at 30 °C.

A (mercaptomethyl)styrene/styrenesulfonate (PSSA/PTMS) copolymer having a 65% thiol concentration adsorbed to gold is shown in Figure 3. The surface composition represents a monolayer of an ion-exchanging polymer. The adsorbance is lower than that observed with the neutral polymers in Figure 2 but is consistent with the high density of thiols. It is noteworthy that the chemisorption is apparently strong enough to overcome the electrostatic repulsion of the surface, although the process may also be thought of as competition between thiol and chloride for surface sites. When adsorption is complete, much of the surface chloride is probably displaced. The density of surface sulfur (using eq 1, $f = 0.9$ and surface roughness = 1.7) is 3.5×10^{14} cm^{-2}, corresponding to an area of 28 Å^2/ft. This value is close to the maximum packing density for a benzyl group[52] (a van der Waals radius of about 3 Å would yield an area of 36 Å^2).

Surface analysis (ESCA) was performed on mechanically polished gold substrates with adsorbed PSSA/PTMS copolymer, as shown in Figure 4. Well-resolved sulfur peaks at 161 and 168 eV binding energy correspond to thiol (and thiolate) sulfur, and sulfonate sulfur, respectively. For six samples the average ratio of thiol to sulfonate sulfur signals was 2.5 with a standard deviation of ±40%. The scatter in data may be due to the use of polished gold foils as substrates instead of evaporated gold. The stability of monolayers under radiation is of concern. For a particular sample,

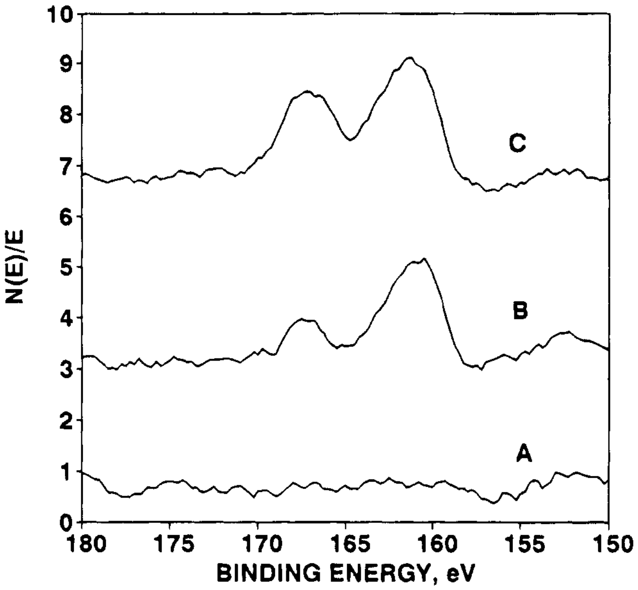


Figure 4. ESCA spectra of the sulfur 2p region for 35/65 poly(styrenesulfonate-*co*-(mercaptomethyl)styrene) adsorbed on gold: (A) background gold; (B) 75° takeoff angle; (C) 15° takeoff angle.

measurement times of 1 h yielded the same relative peak areas (albeit with more noise) as 24 h exposures, leading us to conclude that no significant degradation of thiols occurred under our conditions. At lower takeoff angles,[53] where the depth probed by ESCA is shallower, the sulfonate sulfur is enhanced. Spectra B and C were recorded at 75 and 15°, for example. Using an electron mean free path of 13 Å for S_{2p}, escape depths of 37 and 10 Å, respectively, may be calculated for these takeoff angles.[54] A surface coverage of 1.8×10^{-7} g cm^{-2} (limiting coverage from Figure 3 divided by surface roughness) and an assumed density of 1.2 g cm^{-3} gives an adsorbed film thickness of 15 Å. The observed angle dependence thus indicates that the sulfonate groups are sticking out from the surface, whereas the thiol (thiolate) sulfurs are buried in the adsorbed layer, which is to be expected if they are responsible for surface binding. The expulsion of sulfonates to the film surface is a consequence of the same type of crowding-out effect seen in adsorbed block copolymers,[13-17] where nonadsorbing segments adopt a brushlike conformation.

Experimental Section

Materials. Ethyl alcohol was distilled from Mg/I_2 complex.[55] Anhydrous dimethylformamide (DMF) (Aldrich), octadecanethiol (Aldrich), thiourea (Fisher), and 4-(chloromethyl)styrene (Kodak) were used as received. Tetrahydrofuran (THF) was distilled from sodium benzophenone. Poly(styrenesulfonic acid) (Scientific Polymer Products), M_n = 70 000, was dialyzed against distilled water with 12 000 molecular-weight-cutoff dialysis tubing.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 250 and Varian 300 MHz FTNMR spectrometers. IR spectra were recorded on a Nicolet-520 FTIR spectrometer. UV−vis spectra were recorded on a Shimadzu UV-260 spectrometer. Elemental analysis was performed at Atlantic Microlab, Atlanta, GA. Melting points are uncorrected. DSC was conducted on a DuPont 9100 thermal analyzer. DSC thermograms were run by first preheating the samples to 180 °C for 3 min and rapidly cooling under a nitrogen atmosphere. Data were collected during second heating runs at a heating rate of 5 °C/min. The molecular weights and molecular weight distributions of polymers were determined by gel permeation chromatography on a Perkin-Elmer LC 250 solvent delivery system fitted with an LC 290 UV detector. A Beckman 7.8 mm × 30 cm styrene−divinylbenzene cross-linked Spherogel column was used for the analysis with THF or DMF at a flow rate of 1 mL/min. The retention times were calibrated against standard monodisperse polystyrene samples. ESCA analyses were carried out with a Perkin-Elmer PHI 5100 surface analysis system operating at $<2 \times 10^{-9}$ Torr base pressure and with Mg Kα (1253.6 eV) radiation. The acquisition time was typically *ca.* 24 h. Substrates for ESCA were 1 cm × 1 cm pieces of gold foil (99.9%) polished with successively finer grades of alumina (down to 0.05 μm) and cleaned with freshly prepared "piranha" solution (3:1, concentrated H_2SO_4:30% H_2O_2; *caution*; piranha reacts violently with organic compounds and should not be stored in closed containers).

The quartz crystal microbalance employed has been described previously.[32,56] The apparatus consisted of a quartz oscillator having freshly-evaporated gold contact pads to which polymers adsorb. The frequency is measured continually while a small (1−5 mL) aliquot of polymer is injected into 30 mL of stirred solvent thermostated to 30 ± 0.1 °C. The adsorbed mass, Δm, is related to the frequency change, Δf, through the Sauerbrey equation:[57]

$$\Delta f = -2f_o^{\,2}\Delta m/A(\varrho_q\mu_q)^{1/2}$$

where f_o is the resonant frequency of the unloaded crystal, A is the area of the electrode, μ_q is the shear modulus of quartz (2.947×10^{11} g cm^{-1} s^{-2}), and ϱ_q is the density of quartz (2.648 g cm^{-2}).

The stability in frequency was optimized to better than 1 Hz h^{-1}, which translates to a detection limit of 0.2 mg m^{-2}.

Counting of radiolabeled polymers was accomplished by placing the dry polymer on a piece of plastic scintillator and determining the activity with a photomultiplier connected to a counter. Details of this apparatus are provided in ref 58.

N-Octadecanethiol ($C_{18}H_{38}S$) was used to verify the performance of the QCM and to compare the behavior of a well-characterized thiol with that of the thiol-containing polymers.

Synthesis. [(Amidinothio)methyl]styrene Hydrochloride. *p*-(Chloromethyl)styrene (10 g, 0.065 mol) and thiourea (12 g, 0.078 mol) were refluxed in 150 mL of a 1:1 mixture of ethanol and acetone for 18 h. After the mixture was concentrated under reduced pressure, the white precipitate obtained was washed with acetone to remove starting materials. The product was purified by dissolving in water and precipitating in acetone. Yield: 12 g (81%). Mp: 162 °C. ^{1}H NMR (DMSO-d_6): δ 4.55 (2H, S), 5.28 (1H, d, J = 10.1 Hz), 5.84 (1H, d, J = 17.7 Hz), 6.68−6.78 (1H, q, J = 10.1 and J = 17.7 Hz). ^{13}C NMR (DMSO-d_6): δ 34.0 ($-CH_2$), 114.8 ($CH_2=$), 125.6, 169.2 ($>C=NH$). Anal. Calc for $C_{10}H_{13}N_2SCl$: C, 52.5; H, 5.68; N, 12.3; S, 14.0; Cl, 15.5. Found: C, 52.7; H, 5.7; N, 12.2; S, 14.0; Cl, 15.5.

(Mercaptomethyl)styrene was synthesized according to literature methods.[59]

Polymerization of 4-[(Amidinothio)methyl]styrene Hydrochloride. Monomer (2 g) and 100 mg of AIBN were dissolved in 10 mL of ethanol in a polymerization tube which was sealed under vacuum after repeated freeze−pump−thaw cycles. Polymerization was carried out at 55 °C. The gel obtained was washed with ethanol. The polymer was purified by dissolving it in a minimum quantity of water and reprecipitating with THF. ^{1}H NMR showed the complete disappearance of vinylic protons and the appearance of new aliphatic protons at about 2 ppm (broad peak). ^{13}C NMR (DMSO-d_6): δ 34 ($-CH$), 114.8 ($CH_2=$), 125.6 and 126.5 ($CH=$ ring), 135.5 and 136.0 ($-C=$ ring), 169.2 ($>C=NH$). Anal. Calc for $\{(C_{10}H_{13}N_2SCl)\cdot H_2O\}_n$: C, 48.7; H, 6.1; N, 11.4; S, 13.0; Cl, 14.4. Found: C, 48.6; H, 6.3; N, 11.2; S, 12.6; Cl, 14.2.

Poly(4-[(amidinothio)methyl]styrene hydrochloride) from Poly((chloromethyl)styrene). Poly(4-[(amidinothio)methyl]styrene) was synthesized from 50 000 molecular-weight poly((chloromethyl)styrene) and thiourea following the procedure reported in the literature.[33,60] Yield: *ca.* 90%. Radiolabeled polyelectrolyte was made using [^{14}C]thiourea (specific activity = 0.1 Ci mol^{-1}, New England Nuclear). The ^{14}C belonging to the thiourea is lost from the polymer on hydrolysis with base (second step, Scheme 1).

Conversion of Poly(4-[(amidinothio)methyl]styrene hydrochloride) to Poly(mercaptomethyl)styrene). Polymer (0.500 g) dissolved in 75 mL of water was warmed to 55–60 °C under argon. In a separate flask 1.5 g of sodium hydroxide was dissolved in deionized water under argon. The thoroughly-purged base was added to the polyelectrolyte solution dropwise under a blanket of argon. A precipitate formed initially which slowly dissolved on further addition of base (as the thiolate salt formed). The reaction mixture was allowed to stand at 50 °C for 18 h and was then quenched with deoxygenated dilute HCl. The resulting precipitate was filtered, washed with distilled water, and dried. IR (KBr): 3051, 3021, 2924, 2848, 2560 (S–H stretch), 1603, 1585, 1468, 797, 704 cm^{-1}.

Styrene/(Mercaptomethyl)styrene Copolymers. PS/% SH. Styrene (10 mL), an appropriate amount of 4-[(amidinothio)methyl]styrene hydrochloride, AIBN (10 mg), and DMF (10 mL) were charged into a polymerization tube which was sealed after degassing. After the desired conversion (generally <20%) the polymer was precipitated in ethanol or hexane. Polymer was purified by reprecipitation from THF. The amidinothio groups were hydrolyzed in THF under argon with aqueous NaOH, and the product was reprecipitated from THF. Anal. Calc for $(C_9H_{10}S)_{0.054}(C_8H_8)_{0.946}$ ("5% copolymer"): C, 90.8; H, 7.6; S, 1.62. Found: C, 90.7; H, 7.7; S, 1.66. Calc for $(C_9H_{10}S)_{0.0082}(C_8H_8)_{0.992}$ ("1% copolymer"): C, 92.1; H, 7.7; S, 0.25. Found: C, 90.8; H, 7.7; S, 0.22.

4-[(Amidinothio)methyl]styrene:4-Styrenesulfonate Complex. Amidinothio salt (2.1 g) in 25 mL of water was added to 2 g of 4-styrenesulfonic acid (sodium salt) in 25 mL of water at 5 °C. The white precipitate obtained was stirred vigorously. The reaction mixture was warmed to room temperature and stirred for 2 h. The precipitate was filtered, washed with cold water, and dried under vacuum at 50 °C. Yield: 3.0 g (90%). Mp: 158–159 °C. 300 MHz ^{1}H NMR (DMSO-d_6): δ 4.45 (2H, S, Ar–CH_2), 5.27, 5.83 (2H, dd, J = 11.1 and 17.7 Hz, =CH_2), 6.67–6.77 (1H, dd, J = 11.1 and 17.7 Hz, =CH), 7.36–7.58 (4H, dd, Ar), 9.05 (3H, b, NH=C–NH_2). 75 MHz ^{13}C NMR (DMSO-d_6): δ 39.9 (Ar–CH_2), 115.0 (C1), 125.7, 126.0 (C9, C10), 126.7 (C4) 129.9 (C5), 134.7 (C6), 136.2 (C2), 136.4 (C13), 137.1 (C3), 137.6 (C11), and 169.4 (C7). Anal. Calc: C, 57.4; H, 5.3; N, 7.4; S, 17.0. Found: C, 57.5; H, 5.3; N, 7.5; S, 17.0.

Poly(4-styrenesulfonate-*co*-4-[(amidinothio)methyl]-styrene). PSSA/PTMS. Polymerization was carried out in DMF or methanol using AIBN as a radical initiator as described above. The cross-linked polymer obtained was washed with hot methanol to remove any unreacted monomer. The cross-linked polymer was then hydrolyzed by suspending it in water and adding deoxygenated NaOH solution. After the addition of base, the polymer dissolved completely and the clear solution obtained was allowed to reflux under argon for 3 h. The reaction was quenched with excess dilute HCl_{aq}. The product was purified by dialysis against dilute HCl and then water, using 12 000 molecular-weight-cutoff dialysis tubing. A transparent colorless film was cast from aqueous solution. IR (KBr): 3429, 3037, 2857, 2560 (S–H), 1642, 1510, 1495, 1124, 1037, 829 cm^{-1}. Anal. Calc for $\{(C_8H_7SO_3H)_{0.35}(C_9H_{10}S)_{0.65}(H_2O)_{0.7}\}_n$ with 5.7 wt % NaCl: C, 56.1; H, 5.7; S, 17.3; O, 15.1; Na, 2.2. Found: C, 56.5; H, 5.9; S, 16.3; O, 15.6; Na, 2.2.

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